

## Feasibility of dibromochloropropane (DBCP) and trichloroethylene (TCE) adsorption onto activated carbons made from nut shells of different almond varieties

K. Thomas Klasson<sup>a,\*</sup>, Craig A. Ledbetter<sup>b</sup>, Lynda H. Wartelle<sup>a</sup>, Sarah E. Lingle<sup>a</sup>

<sup>a</sup> U.S. Department of Agriculture, Agricultural Research Service, Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA

<sup>b</sup> U.S. Department of Agriculture, Agricultural Research Service, San Joaquin Valley Agricultural Sciences Center, 9611 S. Riverbend Ave., Parlier, CA 93648, USA

### ARTICLE INFO

#### Article history:

Received 14 August 2009

Received in revised form 2 November 2009

Accepted 4 November 2009

#### Keywords:

Activated carbon

Almond shells

Steam activation

Trichloroethylene

Dibromochloropropane

### ABSTRACT

Steam-activated carbons were made from shells from five different almond varieties ('Nonpareil,' 'Padre,' 'Tuono,' '23-122,' and 'Y120-74') and from a mix of almond types. The purpose of the work was to evaluate if the composition of shells had any effect on the performance of the final product. The shells contained the same level of cellulose, but differed in their lignin and hemicellulose composition. The yield of carbon from the shells ranged from 20% to 23.5%, indicating a loss of about 80% of initial mass. Regardless of the composition, the performance of the activated carbons made from the shells was very similar in a feasibility study. The carbons were found to have a capacity of 100–105 mg/g of carbon for the two contaminants tested (dibromochloropropane and trichloroethylene). The finding that the activated carbons performed equally well, regardless of source of almond shells, suggest that that carbons could be made from almonds shells with consistent quality.

Published by Elsevier B.V.

### 1. Introduction

Dibromochloropropane (1,2-dibromo-3-chloropropane or DBCP) and trichloroethylene (1,1,2-trichloroethene or TCE) are dense liquids which are regulated by U.S. Environmental Protection Agency (EPA) under the National Primary Drinking Water Regulations (Anon., 2002) and TCE is also considered a priority pollutant (Anon., 2008c). The maximum contaminant levels allowed are 0.2 and 5 µg/L for DBCP and TCE, respectively, in community and non-transient, non-community water systems (Anon., 2002). DBCP was primarily used as an unclassified nematicide for vegetables and others but is no longer produced in the U.S. Its use in farming contaminates groundwater and aquifers of nearby communities (Wong, 1990; Kloos, 1997) and exposures to DBCP have shown linkage to disease of circulatory system and infertility (Wong et al., 1984; Jensen et al., 2006). TCE is a common industrial solvent and has mainly been used as a degreaser. Due to its prevalent use, it has found its way into soil and groundwater through spills and improper releases (Barbash and Roberts, 1986). The issue of groundwater contamination with TCE is not unique to the U.S. but exists in many countries including Japan and Taiwan (Nakano et al., 2000).

The use of activated carbons for removal of DBCP and TCE is considered best technology treatment technique by EPA (Anon., 2002) and the use of activate carbon as an adsorbent for direct TCE removal from water is well documented (Browne and Cohen, 1990; Zytner, 1992). Activated carbon columns have been used successfully to remove DBCP in California (Wong, 1990).

A variety of sources may be considered for activated carbon generation; coal, wood char, and agricultural by-products (Heschel and Klose, 1995). Unlike coal and to some extent wood, agricultural by-products are abundant, low cost and renewable. In this paper, we describe the performance of activated carbons made via steam activation of almond shells from different almond varieties. Steam activation is the most common method of producing activated carbons, but activated carbon production from almond shells using carbon dioxide activation (Rodriguez-Reinoso et al., 1982; Rivera-Utrilla and Ferro-Garcia, 1987; Ferro-García et al., 1988, 1990; Toles et al., 2000c), steam activation (Gergova et al., 1992, 1994; Heschel and Klose, 1995; Toles et al., 2000c; Wartelle and Marshall, 2001), acid activation (Johns et al., 1999; Toles et al., 2000a,b), and chemical activation (Bevlá et al., 1984a,b; Balci et al., 1994) has previously been investigated. However, none of these studies focused on preparation of activated carbons from shells of different varieties of almonds.

Measured by any of several different means, almond production has increased rapidly over the last several decades. Worldwide, harvested area has increased from 1.1 million ha in

\* Corresponding author. Tel.: +1 504 2864511; fax: +1 504 2864367.

E-mail address: [Thomas.Klasson@ars.usda.gov](mailto:Thomas.Klasson@ars.usda.gov) (K. Thomas Klasson).

1977 to 1.8 million ha in 2007 (FAOSTAT, 2009). In California, where standing orchards accounted for approximately 219,000 ha in 1998, acreage now stands at 299,000 ha (Anon., 2008a). During the same period, California orchards have consistently produced 75% of the world's almond tonnage, and industry handlers have reduced prior year crop carry-in through rising demand for almonds in both domestic and export markets. Valued at 1.88 billion USD, almond kernels were first among US specialty crop exports during 2007 (Anon., 2008a).

Increased almond acreage and utilization has led to similar increases in production by-products. Almond hulls are utilized effectively as a palatable feedlot supplement for cattle. A small proportion of almond shells are (or could be) utilized for diverse industrial applications (Mayeux and Ruby, 1999; Toles et al., 2000b,c; Bansode et al., 2003; Lao and Jiménez, 2004; Rodríguez-Lorenzo and Ferreira, 2004), but the majority currently finds a no more suitable use than as feedstock for energy co-generation. The substantial production area of California's almond orchards and kernel marketing classes of the various varieties provides significant tonnage of almond shells that are variety specific. 'Nonpareil,' the predominant (37% of production) variety grown in California (Anon., 2008b), generates from 83,000 to 95,000 metric tons of shells annually, based on a 65–60% kernel percentage, respectively (Ak et al., 2005; Ayadi et al., 2006). Significant almond shell volumes from other specific varieties are available, as the five most widely planted varieties ('Nonpareil,' 'Carmel,' 'Butte,' 'Monterey,' and 'Padre') account for 79% of production (Anon., 2008b).

The development of high-volume agricultural wastes into value-added by-products requires annually consistent and uniform feedstocks for the given process. Previous studies have demonstrated variability in almond shell chemical composition (Demirbas, 2002; Font et al., 1988; Pou-Llínas et al., 1990; Wartelle and Marshall, 2001), perhaps due to differences in the varieties of almond shells used in the separate analyses. Significant differences in specific physical characteristics of almond shells were identified through planned varietal evaluations (Aktas et al., 2007; Ledbetter, 2008). Recently, radical scavenging capacity was found to vary significantly in the almond shell evaluations of 18 genotypes (Sfahlan et al., 2009). Systematic screening of varietal almond shells provides valuable information in the identification of those shell types having a specific composition or properties most appropriate to a given industrial application. In this study, almond shells of three distinct varieties ('Nonpareil,' 'Padre' and 'Tuono'); two advanced breeding lines ('23-122' and 'Y120-74'); and a mixture of varieties were evaluated in chemical composition; and granular activated carbons generated from them were compared for their abilities to adsorb hydrocarbons.

## 2. Materials and methods

### 2.1. Materials

Almond shells utilized in this study were obtained from almonds grown in a flood irrigated research orchard of the San Joaquin Valley Agricultural Sciences Center in Parlier, California. Trees were in their eighth to fourteenth year of production when utilized in this study. Nuts were harvested from individual accessions when hull split was at least 80% complete. Almonds were knocked from trees onto polypropylene tarps and sun dried for approximately 5 days. Almond hulls and all foreign matter were then manually removed from the nuts. A research-sized commercial almond cracking unit with interchangeable rollers was used to break apart the almond nuts (Ledbetter and Palmquist, 2006). Soft shell accessions 'Nonpareil' and '23-122' were cracked using rubber rollers whereas serrated steel rollers were used for hard shell accessions ('Padre,' 'Tuono,' and 'Y120-74'). Kernels were then manually removed to

provide clean samples of varietal almond shells. In addition to the individual varieties, a mixture of shells was also included in the study. This mixture of shells came from the cracking of approximately 50 varieties and it may be seen as a 'random' sample from a large almond shelling facility. The shells were milled through a cutting mill (SM2000, Retsch GmbH, Haan, Germany) and sieved to retain the 0.84–2 mm (No. 10–20 sieve) fraction as a result of previous experiments (Lima et al., 2004; Marshall et al., 2007).

The commercial carbon Calgon Filtrasorb 300 (Calgon Carbon Corp., Pittsburgh, PA) was used as delivered for comparison purposes and was used without further milling. Based on manufacturer's information, Filtrasorb 300 is a bituminous coal-based carbon designated for use in removing dissolved organic compounds in potable water (Anon., 2008d).

### 2.2. Experimental methods

Pyrolysis and steam activation were performed in a porcelain evaporating dish (265 mm diameter, CoorsTek, Golden, CO) placed in a high-temperature furnace with retort (Lindberg, Type 51662-HR, Watertown WI) with a void volume of 22 L. The material was heated to 700 °C for 1 h with continuous flow (1.6 L/min) of nitrogen gas. During pyrolysis in an inert atmosphere, the material lose volatiles and gases, chemical bonds are broken and formation of carbonyl, carboxyl groups are noted and the type of reactions that take place are raw material and process dependent (Shafizadeh, 1982; Babu, 2008; Lv et al., 2009). Following the pyrolysis, the furnace temperature was increased to 850 °C and the material was steam activated for 1.5 h by introducing water at a flow rate of 3 mL/min into the nitrogen gas entering into the cavity of the furnace. The activation process involves oxidation and opens the pores and develops the structure (Rodríguez-Reinoso et al., 1982; Bansal and Goyal, 2005). After activation, the furnace contents were allowed to cool overnight with a constant nitrogen gas flow (1.6 L/min). Due to the alkaline nature of these types of activated carbons (Wartelle and Marshall, 2001; Toles and Marshall, 2002), the cooled carbon was washed with 0.1 M HCl at a ratio of approximately 100:1 (w/w, liquid:carbon) for 1 h, then washed over a No. 60 sieve screen (0.25-mm opening) with deionized water to a neutral pH, and finally oven dried at 80 °C. The yield of experimental carbon was noted by how much of the initial shell weight was reduced in the final product.

Adsorption studies for feasibility screening purposes were carried out in 20 mL glass vials using approximately 0.04 g of activated carbon and water containing TCE and DBCP at an initial concentrations of each a nominal 200 mg/L. This concentration is considered exceptionally high but was chosen to challenge the activated carbons, which were assumed to have strong adsorption properties to both contaminants. A high initial concentration also assured that there would be some un-adsorbed material at the end of the experiments. The vials were completely filled to eliminate headspace. The vials were agitated for 48 h at room temperature and the liquid was analyzed for TCE and DBCP.

### 2.3. Analytical methods

The content of cellulose, hemicellulose, and lignin in the ground almond hulls was determined according to the method of Goering and Van Soest (1970) using an Ankom A200 fiber analyzer (Ankom Technology, Macedon, NY). Samples ( $0.5 \pm 0.01$  g in sealed fiber bags) were extracted sequentially for 1 h at 100 °C in neutral detergent solution (30 g/L sodium dodecyl sulfate, 50 mM disodium ethylenediamine tetraacetic acid, 18 mM sodium tetraborate decahydrate, 32 mM dibasic sodium phosphate, 10 mL/L triethylene glycol) to remove soluble compounds and acid detergent solution (20 g/L cetyl trimethylammonium bromide, 1N H<sub>2</sub>SO<sub>4</sub>) to remove

hemicellulose. The bags were then immersed in 72% H<sub>2</sub>SO<sub>4</sub> for 3 h with frequent agitation to solubilize cellulose, leaving ash and lignin. The samples were dried at 100 °C overnight after each step; the difference in weight before and after each step was used to calculate the content of each component. After the final extraction, the residue was combusted for 6 h at 600 °C in a high-temperature furnace to determine ash.

Surface areas for the activated carbons were determined using a Quantachrome NOVA automated nitrogen gas adsorption system (Quantachrome Instruments, Boynton Beach, FL). Samples were run in duplicate and specific surface areas were taken from the adsorption isotherms at –196 °C using the Brunauer–Emmett–Teller (BET) equation (Brunauer et al., 1938). The micropore (<2 nm diameter pores) areas were calculated using t-plots derived from the Nova 2000 software. Similarly, using the Nova 2000 AS1win software, the mesopore (2–50 nm diameter pores) areas were calculated using the quenched solid density functional theory (Neimark et al., 2009).

Attrition was determined by placing 3 g of 0.42–1.00 mm granular activated carbon in a 250-mL Erlenmeyer flask together with ten 5-g-glass marbles in continuous agitation at 200 rpm in an Innova (New Brunswick Scientific, NJ) water bath shaker for 15 min at 25 °C. Attrition was calculated as the percentage of the carbon retained by a 0.42-mm-size sieve.

Following contact of liquid (containing TCE and DBCP) and activated carbons, a 10-mL aliquot was filtered using a 0.45-μm-pore-size syringe filter into a 20-mL sample vial for headspace analysis. Four grams of anhydrous sodium sulfate was added to saturate the solution and to drive the organic compounds into the headspace for solid-phase microextraction (SPME) analysis using a carboxen/polydimethyl-siloxane/divinylbenzene SPME fiber (Supelco, Bellefonte, PA). The SPME fiber adsorbed the analytes for 15 min with agitation at 40 °C using a CTC Combi PAL autoinjector (Leap Technologies, Carrboro, NC) on a Agilent Model 6890N gas chromatograph (GC) with a Model 5973N mass spectrophotometer (MS) detector (Agilent Technologies, Inc., Santa Clara, CA) to detect the TCE and DBCP. A 30 m × 0.32 μm HP-5ms [(5%-phenyl)-methylpolysiloxane] capillary column from Agilent Technologies was used in the GC. The temperature for the pulsed-splitless injector was 270 °C. The oven temperature was held at 35 °C for 5 min, ramped at 8 °C/min, and held at 110 °C for 2 min. Selective ion monitoring on the mass spectrometer detector (source held at 150 °C and quadrupole at 106 °C) was used to acquire area counts at 95 and 130 *m/z*. Calibration, using 5–6 standards was performed using known concentrations of TCE and DBCP in water and the headspace analysis method and detection limits for TCE and DBCP were 5 μg/L, which was similar to that of Poli et al. (2005).

ANOVA variance analysis ( $P < 0.05$ ) and correlation was done with Microsoft Excel 2003 (Richmond, WA) with post hoc Tukey's honestly significant difference test equations (Walpole and Myers, 1989). In this manner, the data from individual activated carbons could be ranked into groups within which no significant difference could be statistically proven. In some of the manuscript's tables and graphs, letters (e.g., A, B, AB, etc.) indicate the results of the post hoc test; results with the same letter are statistically not different. Thus, results in group A are significantly different than results in groups B and C, while they are not significantly different than results in group AB, and so on.

### 3. Results and discussion

The composition of the almond shells are shown in Table 1. As is noted, the pure varieties 'Tuono' and its breeding partner, 'Y120-74', had the highest lignin content, together with the shell mixture (from about 50 varieties). 'Nonpareil' and its breeding partner '23-122' had the lowest lignin content. There was no significant difference in the amount of ash or cellulose in the shells from the

**Table 1**

Composition of shells of different almond varieties. The compositional analysis was performed in duplicate. The superscript letters indicate the result of Tukey's post hoc statistical test.

	Ash	Lignin	Cellulose	Hemicellulose
Nonpareil	5.6 <sup>A</sup>	204 <sup>A</sup>	404 <sup>A</sup>	242 <sup>AB</sup>
Padre	5.9 <sup>A</sup>	262 <sup>B</sup>	425 <sup>A</sup>	286 <sup>D</sup>
Tuono	5.8 <sup>A</sup>	289 <sup>C</sup>	383 <sup>A</sup>	301 <sup>E</sup>
23-122	6.2 <sup>A</sup>	246 <sup>B</sup>	439 <sup>A</sup>	243 <sup>BC</sup>
Y120-74	5.8 <sup>A</sup>	324 <sup>D</sup>	404 <sup>A</sup>	235 <sup>A</sup>
Mixed	5.7 <sup>A</sup>	305 <sup>CD</sup>	393 <sup>A</sup>	251 <sup>C</sup>
Standard error	0.9	9	15	8

different varieties but difference was noted in the hemicellulose and lignin contents of the shells.

The production of activated carbons from shells of the different almond varieties, resulted in a final carbon yield of 20–23.5%, based on the final amount of sorbent and the initial amount of shells. This means that 76.5–80% of the initial mass was gasified during the pyrolysis cycle. This yield compares well with previous studies using similar activation conditions (Toles et al., 2000c). While no attempt was made to characterize the furnace off gases, typical biomass pyrolysis gases contain condensables and low-molecular weight gases, such as CO, CO<sub>2</sub>, CH<sub>4</sub>, etc. (Becidan et al., 2007; de Wild et al., 2009). The total specific BET surface area ranged from 549 to 628 m<sup>2</sup>/g for the experimental carbons, while the micropore surface areas ranged from 445 to 562 m<sup>2</sup>/g (see Table 2). Some statistical difference in the measured surface areas was noted for the experimental carbons, but statistical test for correlation between fraction lignin and hemicellulose and surface area indicated that the variability in composition of the shells did not result in any significant influence the surface area. The surface areas the experimental carbons were approximately 25% lower than the commercial carbon (see Table 2).

The tendency for the granular activated carbons to break into smaller pieces (during attrition tests) was different for the different almond varieties. In Fig. 1, the carbon most likely to break, or to get crushed, was variety '23-122.' It was curious to find that the attrition of the GAC from variety '23-122' was over four times that of the GACs for the other pure almond varieties, but this experiment was repeated and confirmed. Thus, it must be concluded that activated carbon solely made from the '23-122' almond variety would not be suitable for application where a lot of stress is put on the granular material (e.g., large scale packed columns). The experimental activated carbon made from the mixed shells was as likely to break as the commercial carbon.

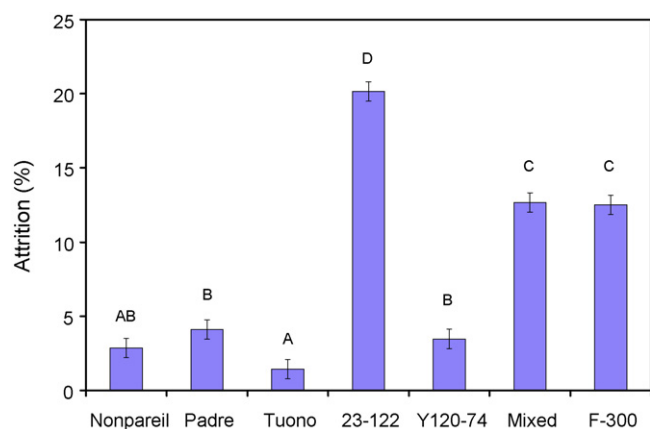
The adsorptive capacity of the carbons was tested with the target compounds DBCP and TCE at each a nominal 200 mg/L and the results are shown in Figs. 2 and 3. The data represent triplicate experiments for each activated carbon type. The figure show that the activated carbons made from the nut shells were able to adsorb approximately 100 mg DBCP per gram of carbon, regardless from which of the almond variety the shell came. The commercial carbon

**Table 2**

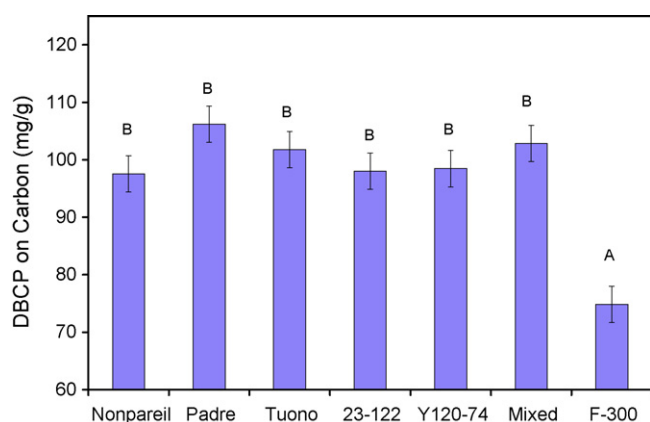
Surface areas of experimental and commercial carbons. The surface area determination was performed on duplicate samples and the superscript letters indicate the results of Tukey's post hoc test.

	BET (m <sup>2</sup> /g)	Micropores (m <sup>2</sup> /g)	Mesopores (m <sup>2</sup> /g)
Nonpareil	549 <sup>A</sup> ± 9 <sup>a</sup>	517 <sup>CB</sup> ± 6	1 <sup>A</sup> ± 4
Padre	560 <sup>AB</sup> ± 4	445 <sup>A</sup> ± 6	18 <sup>B</sup> ± 4
Tuono	563 <sup>AB</sup> ± 4	490 <sup>B</sup> ± 1	11 <sup>AB</sup> ± 4
23-122	575 <sup>AB</sup> ± 4	522 <sup>C</sup> ± 3	6 <sup>AB</sup> ± 4
Y120-74	587 <sup>B</sup> ± 6	525 <sup>C</sup> ± 6	16 <sup>AB</sup> ± 4
Mixed	628 <sup>C</sup> ± 18	562 <sup>D</sup> ± 23	8 <sup>AB</sup> ± 4
Calgon F-300	900 <sup>C</sup> ± 34	791 <sup>E</sup> ± 27	34 <sup>C</sup> ± 4

<sup>a</sup> Term indicates the standard error of the mean value.

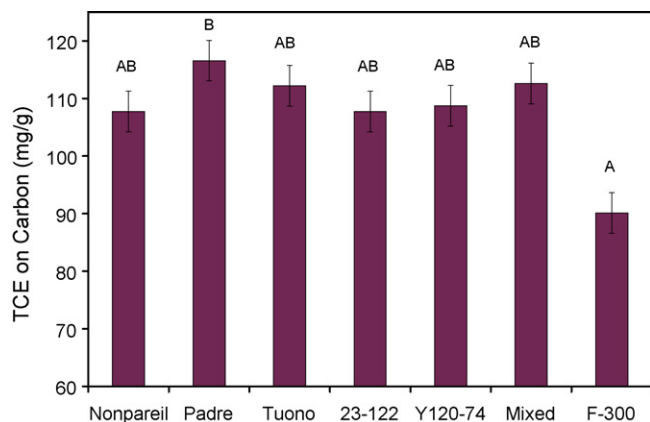


**Fig. 1.** Results from attrition studies. The experiments were conducted in duplicates. The error bars indicate standard errors (based on pooled standard deviation) and the letters above the bars show the results of the Tukey's post hoc statistical test.



**Fig. 2.** DBCP uptake by commercial activated carbon and activated carbons made from different almond variety nutshells. The error bars indicate standard errors (based on pooled standard deviation) and the letters above the bars show the results of the Tukey's post hoc statistical test.

did almost as well but was statistically less effective in removing DBCP; no statistical difference was noted between the experimental carbons. Little data is available for DBCP adsorption on carbon but some data suggest that 50–60 mg DBCP can be adsorbed by Calgon Filtrasorb 300 (Dobbs and Cohen, 1980; Wong, 1990) at a final equilibrium DBCP concentration of 1 mg/L. The value com-



**Fig. 3.** TCE uptake by commercial activated carbon and activated carbons made from different almond variety nutshells. The error bars indicate standard errors (based on pooled standard deviation) and the letters above the bars show the results of the Tukey's post hoc statistical test.

pare very well with the data obtained for the F-300 carbon in our studies (Fig. 2) at similar equilibrium concentrations.

The uptake of TCE of the carbons was similar to the DBCP uptake and the material adsorbed approximately 110 mg TCE per g carbon, regardless of the source of the almond shells used for the carbons. While there was a statistical difference with the best performing experimental carbon and the commercial carbon, the difference was small. The results from the studies conducted here (Fig. 3) compare well with results in the literature for steam-activated carbon. Karanfil and Dastgheib (2004) and Urano et al. (1991) showed that Calgon F-400 adsorbed approximately 100 mg of TCE/g of carbon. O'Brien and Stenzel (1984) showed that Calgon F-300 could adsorb 60 and 100 mg of TCE/g of carbon at equilibrium TCE concentration of 1 and 4 mg/L, respectively. While these studies noted similar capacities to the ones obtained in our studies, other studies by Yu and Chou (2000) found that 30 mg of TCE could be adsorbed onto 1 g of Calgon F-400 contained in a column, treating TCE-containing water at a concentration of 1 mg/L. Zytner (1992) predicted that 82 mg of TCE would be adsorbed onto Westvaco Nuclear activated carbon at an equilibrium concentration of 1 mg TCE/L.

The results from current studies suggest that it is feasible to use almond-shell-based activated carbons for treatment of water contaminated with DBCP and TCE. The results also give an indication of the uptake capacity of DBCP and TCE; however, engineering studies would be required before final recommendations could be made. The cost of producing steam-activated carbons from almond shells has previously been estimated at \$1.54/kg of carbon (Toles et al., 2000c). The production cost for commercial carbons are not known but historical average prices have been \$1.79–2.09/kg of carbon during 2000–2005 (Kirschner, 2006). Thus, it appears that activated carbons made from agricultural resources may have potential for commercial application.

#### 4. Conclusion

Activated carbons were successfully produced from shells of different almond varieties. The compositional differences in the almond shells did not translate to any significant differences in the performance of the activated carbon in respect to uptake of TCE and DBCP. This finding suggests that almond shells could serve a source of raw material for activated carbon manufacture and regardless of variety, would produce a reliable product. The structural integrity of the activated carbons made from almond shells was better than or equal to that of the commercial control carbon, with one exception—carbon made from the shells of the variety known as '23-122' produced a noticeable softer activated carbon.

#### Acknowledgement

The mention and use of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

#### References

- Ak, B.E., Kuzdere, H., Kaska, N., 2005. An investigation on phenological and pomological traits of some almond cultivars grown at Ceylanpinar State farm in Turkey. *Options Méditerran.* A 63, 43–48.
- Aktas, T., Polat, R., Atay, U., 2007. Comparison of mechanical properties of some selected almond cultivars with hard and soft shell under compression loading. *J. Food Proc. Eng.* 30 (6), 773–789.
- Anon., 2002. Maximum contaminant levels for organic contaminants. In: Code of Federal Regulations. 40CFR141.61, pp. 426–428.
- Anon., 2008a. Almond Almanac 2008. Almond Board of California, Modesto, CA.
- Anon., 2008b. Almond Industry Position Report 2007–2008 Crop Year. Almond Board of California, Modesto, CA.
- Anon., 2008c. New source performance standards (NSPS). In: Code of Federal Regulations. 40CFR423.15, pp. 651–654.



- Anon., 2008d. Filtrasorb 300 Granulated Activated Carbon for Municipal Specifications. CPM-PB1042A-0108. Calgon Carbon Corporation, Pittsburgh, PA.
- Ayadi, M., Ghrab, M., Gargouri, K., Elloumi, O., Zribi, F., Ben Mimoun, M., Boulares, C.H., Guedri, W., 2006. Kernel characteristics of almond cultivars under rainfed conditions. *Acta Hort.* (ISHS) 726, 377–382.
- Babu, B.V., 2008. Biomass pyrolysis: a state-of-the-art review. *Biofuels Bioprod. Bioref.* 2 (5), 393–414.
- Balci, S., Doğru, T., Yücel, H., 1994. Characterization of activated carbon produced from almond shell and hazelnut shell. *J. Chem. Tech. Biotechnol.* 60, 419–426.
- Bansal, R.C., Goyal, M., 2005. *Activated Carbon Adsorption*. Taylor & Francis, Boca Raton, FL, pp. 3–7.
- Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M., Portier, R.J., 2003. Adsorption of volatile organic compounds by pecan shell- and almond shell-based granular activated carbons. *Bioresour. Technol.* 90, 175–184.
- Barbash, J., Roberts, P.V., 1986. Volatile organic chemical contamination of groundwater resources in the U.S. *J. WPCF* 58 (5), 343–348.
- Becidan, M., Skreiberg, Ø., Hustad, J.E., 2007. Products distribution and gas release in pyrolysis of thermally thick biomass residues samples. *J. Anal. Appl. Pyrolys.* 78 (1), 207–213.
- Bevlá, F.R., Rico, D.P., Gomis, A.F.M., 1984a. Activated carbon from almond shells. Chemical activation. 1. Activating reagent selection and variables influence. *Ind. Eng. Chem. Prod. Res. Dev.* 23, 266–269.
- Bevlá, F.R., Rico, D.P., Gomis, A.F.M., 1984b. Activated carbon from almond shells. Chemical activation. 2.  $\text{ZnCl}_2$  activation temperature influence. *Ind. Eng. Chem. Prod. Res. Dev.* 23, 269–271.
- Browne, T.E., Cohen, Y., 1990. Aqueous-phase adsorption of trichloroethene and chloroform onto polymeric resins and activated carbon. *Ind. Eng. Chem. Res.* 29 (7), 1338–1345.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60 (2), 309–319.
- Demirbas, A., 2002. Fuel characteristics of olive husk and walnut, hazelnut, sunflower, and almond shells. *Energy Sour.* 24 (3), 215–221.
- de Wild, P.J., den Uil, H., Reith, J.H., Kiel, J.H.A., Heeres, H.J., 2009. Biomass valorization by staged degasification: A new pyrolysis-based thermochemical conversion option to produce value-added chemicals from lignocellulosic biomass. *J. Anal. Appl. Pyrolys.* 85 (1), 124–133.
- Dobbs, R.A., Cohen, J.M., 1980. Carbon Adsorption Isotherms for Toxic Organics. EPA-600/8-80-023. U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Cincinnati, OH.
- FAOSTAT, 2009. Food and agriculture commodities production. Food and Agriculture Organization of United Nations, Last accessed July 2009. <http://faostat.fao.org>.
- Ferro-García, M.A., Rivera-Utrilla, J., Rodríguez-Gordillo, J., Bautista-Toledo, I., 1988. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. *Carbon* 26 (3), 363–373.
- Ferro-García, M.A., Rivera-Utrilla, J., Bautista-Toledo, I., Mingorance, M.D., 1990. Removal of lead from water by activated carbons. *Carbon* 28 (4), 545–552.
- Font, R., Marcilla, A., Devesa, J., Verdú, E., 1988. Gaseous hydrocarbons from flash pyrolysis of almond shells. *Ind. Eng. Chem. Res.* 27, 1143–1149.
- Gergova, K., Galushko, A., Petrov, N., Minkova, V., 1992. Investigation of the porous structure of activated carbons prepared by pyrolysis of agricultural by-products in a stream of water vapor. *Carbon* 30 (5), 721–727.
- Gergova, K., Petrov, N., Eser, S., 1994. Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. *Carbon* 32 (4), 693–702.
- Goering, H.K., Van Soest, P.J., 1970. Forage Fiber Analysis (Apparatus, Reagents, Procedures, and Some Applications). Agricultural Handbook No. 379. U.S. Department of Agriculture, Agricultural Research Service, Washington, DC.
- Heschel, W., Klose, E., 1995. On the suitability of agricultural by-products for the manufacture of granular activated carbon. *Fuel* 74 (12), 1786–1791.
- Jensen, T.K., Bonde, J.P., Joffe, M., 2006. The influence of occupational exposure on male reproductive function. *Occup. Med.* 56, 544–553.
- Johns, M.M., Marshall, W.E., Toles, C.A., 1999. The effect of activation method on the properties of pecan shell-activated carbons. *J. Chem. Technol. Biotechnol.* 74, 1037–1044.
- Karanfil, T., Dastgheib, S.A., 2004. Trichloroethylene adsorption by fibrous and granular activated carbons: aqueous phase, gas phase, and water vapor adsorption studies. *Environ. Sci. Technol.* 38 (22), 5834–5841.
- Kloos, H., 1997. Trichloroethylene, tetrachloroethylene, nitrates, and other chemicals in well water in the Fresno-Clovis metropolitan area. *Arch. Environ. Health* 52 (5), 348–354.
- Kirschner, M., 2006. Activated carbon. *Chem. Mark. Rep.* 270 (2), 34.
- Lao, M.T., Jiménez, S., 2004. Evaluation of almond shell as a culture substrate for ornamental plants II. *Ficus benjamina*. *Phyton (Buenos Aires)* 73, 79–84.
- Ledbetter, C.A., 2008. Shell cracking strength in almond (*Prunus dulcis* [Mill.] D.A Webb.) and its implication in uses as a value-added product. *Bioresour. Technol.* 99, 5567–5573.
- Ledbetter, C.A., Palmquist, D.E., 2006. Comparing physical measures and mechanical cracking products of 'Nonpareil' almond (*Prunus dulcis* [Mill.] D.A Webb.) with two advanced breeding selections. *J. Food Eng.* 76, 232–237.
- Lima, I.M., Marshall, W.E., Wartelle, L.H., 2004. Hardwood-based granular activated carbon for metals remediation. *J. AWWA* 96 (7), 95–102.
- Lv, D., Xu, M., Liu, X., Zhan, Z., Li, Z., Yao, H., 2009. Effect of cellulose, lignin, alkali, and alkaline earth metallic species on biomass pyrolysis and gasification. *Fuel Proc. Technol.*
- Marshall, W.E., Wartelle, L.H., Akin, D.E., 2007. Flax shive as a source of activated carbon for metals remediation. *Bioresources* 2 (1), 82–90.
- Mayeux, H.J., Ruby, E.C., 1999. Almond shell additive and method of inhibiting sticking in wells. U.S. Patent 5,861,362.
- Nakano, Y., Hua, L.Q., Nishijima, W., Shoto, E., Okada, M., 2000. Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon (GAC). *Water Res.* 34 (17), 4139–4142.
- Neimark, A.V., Lin, Y., Ravikovitch, P.I., Thommes, M., 2009. Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. *Carbon* 47, 1617–1628.
- O'Brien, R.P., Stenzel, M.H., 1984. Combining activated carbon and air stripping. *Pub. Works* 115, 54–58.
- Polli, D., Manini, P., Andreoli, R., Franchini, I., Mutti, A., 2005. Determination of dichloromethane, trichloroethylene and perchloroethylene in urine samples by headspace solid phase microextraction gas chromatography-mass spectrometry. *J. Chromatogr. B* 820 (1), 95–102.
- Pou-Llinas, J., Canellas, J., Driguez, H., Excoffier, G., Vignon, M.R., 1990. Steam pretreatment of almond shells for xylose production. *Carbohydr. Res.* 207 (1), 126–130.
- Rivera-Utrilla, J., Ferro-García, M.A., 1987. Study of cobalt adsorption from aqueous solution on activated carbons from almond shells. *Carbon* 25 (5), 645–652.
- Rodríguez-Lorenzo, L.M., Ferreira, J.M.F., 2004. Development of porous ceramic bodies for applications in tissue engineering and drug delivery systems. *Mater. Res. Bull.* 39, 83–91.
- Rodríguez-Reinoso, F., Lopez-Gonzalez, J., de, D., Berenguer, C., 1982. Activated carbons from almond shells-I preparation and characterization by nitrogen adsorption. *Carbon* 20 (6), 513–518.
- Sfahlan, A.J., Mahmoodzadeh, A., Hasanzadeh, A., Heidari, R., Jamei, R., 2009. Antioxidants and antiradicals in almond hull and shell (*Amygdalus communis* L.) as a function of genotype. *Food Chem.* 115 (2), 529–533.
- Shafizadeh, F., 1982. Introduction to pyrolysis of biomass. *J. Anal. Appl. Pyrolys.* 3 (4), 283–305.
- Toles, C.A., Marshall, W.E., Johns, M.M., 2000a. Activated nutshell carbons from agricultural waste. U.S. Patent 6,033,573.
- Toles, C.A., Marshall, W.E., Johns, M.M., Wartelle, L.H., McAloon, A., 2000b. Acid-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production. *Bioresour. Technol.* 71, 87–92.
- Toles, C.A., Marshall, W.E., Wartelle, L.H., McAloon, A., 2000c. Steam- or carbon dioxide-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production. *Bioresour. Technol.* 75, 197–203.
- Toles, C.A., Marshall, W.E., 2002. Copper ion removal by almond shell carbons and commercial carbons: batch and column studies. *Sep. Sci. Technol.* 37 (10), 2369–2383.
- Urano, K., Yamamoto, E., Tonegawa, M., Fujie, K., 1991. Adsorption of chlorinated organic compounds on activated carbon from water. *Water Res.* 25 (12), 1459–1464.
- Walpole, R.E., Myers, R.H., 1989. *Probability and Statistics for Engineers and Scientists*, 4th ed. Macmillan Publishing Company, New York, p. 486.
- Wartelle, L.H., Marshall, W.E., 2001. Nutshells as granular activated carbons: physical, chemical and adsorptive properties. *J. Chem. Technol. Biotechnol.* 76, 451–455.
- Wong, J.M., 1990. Treatment options for water supplies contaminated with DBCP and other pesticides. *Pub. Works* 121 (7), 78–81 and 115.
- Wong, O., Brocker, W., Davis, H.V., Nagle, G.S., 1984. Mortality of workers potentially exposed to organic and inorganic brominated chemicals, DBCP, TRIS PBB, and DDR. *Br. J. Ind. Med.* 41, 15–24.
- Yu, J.-J., Chou, S.-Y., 2000. Contaminated site remedial investigation and feasibility removal of chlorinated volatile organic compounds from groundwater by activated carbon fiber adsorption. *Chemosphere* 41, 371–378.
- Zytner, R.G., 1992. Adsorption-desorption of trichloroethylene in granular media. *Water Air Soil Pollut.* 65, 245–255.